

Direct Conversion of Alcohols into Thiols

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A simple one-pot reaction between alcohols and 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide (Lawesson's reagent, LR) affords the corresponding thiols, accompanied by dehydration products, alkenes. Treatment of acyclic 1,4-diols with LR gives the 1,3-dienes. *o*-(Dihydroxymethyl)benzene derivatives yield the 1,3-dihydrobenzo[*c*]thiophenes when treated with LR.

2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide (LR), commonly known as Lawesson's reagent, has been used as a powerful, mild, and versatile reagent for a conversion of a wide variety of carbonyls into thiocarbonyl compounds.¹ Lawesson and co-workers described in one of their studies on organophosphorus compounds the formation of *O*-alkyl esters of phosphonodithionic acid by the reaction of alcohols with LR.^{2,3} The synthesis of thiols starting from primary alcohols and P₂S₅ via dialkyl dithionophosphates was reported some time ago.⁴ Until now, no one has reported a direct route to thiols from alcohols. Herein we report a direct conversion of alcohols into thiols using LR.⁵

Results and Discussion

Triphenylmethanol **1a** was treated with 0.5 mole equivalent of LR in 1,2-dimethoxyethane (DME) at room temperature under argon for 15 h to give triphenylmethanethiol **2a** in quantitative yield. At a higher temperature (reflux in toluene), this reaction proceeded more smoothly and was complete in a shorter period (*ca.* 10 min). The alcohols **1b**, **1c**, **1f–h**, **1o** and **1r–v** were similarly converted into the corresponding thiols **2b**, **2c**, **2f–h**, **2o** and **2r–v** when they were treated with LR in toluene under reflux (Table 1). However, treatment of tertiary alcohols **1d**, **1e**, **1i**, **1k** and **1l** and secondary alcohols **1j** and **1q**, which possess an alkyl group at the α -position, with LR gave dehydration products, alkenes **3–10** and **14** as well as the corresponding thiols **2d**, **2e**, **2i–l** and **2q**. The thiols were

produced predominantly at lower temperature. For example, treatment of 1,1-diphenylethanol **1d** with LR in DME at room temperature yielded 1,1-diphenylethanethiol **2d** and 1,1-diphenylethylene **3** in 77 and 13% yield, respectively, while at higher temperature (reflux in toluene) compound **1d** yielded thiol **2d** (7%) and alkene **3** (91%). The dehydration product, 1,1-diphenylethylene **3**, was also obtained when the thiol **2d** was refluxed in toluene in the presence of LR. On the other hand, alkene **3** was not formed when thiol **2d** was refluxed in toluene in the absence of LR. LR also has dehydrating activity. Cyclopropyl alcohols **1m** and **1n** gave the corresponding thiols **2m** and **2n** and the rearranged products **11** and **12** when treated with LR. Allylic alcohols **1o** and **1p** also reacted with LR to yield the thiols **2o** and **2p** and the rearranged product **13**.

As shown in Scheme 1, a plausible mechanism for the formation of the thiols **2** and dehydration products, alkenes **3–10** and **14**, may be envisaged as involving an *O*-alkyl phosphonodithionic acid as an intermediate.³ The nucleophilic attack of the alcohol **1** to a dipolar species of LR, which may be present in solution,⁶ gives an *O*-alkyl phosphonodithionic acid intermediate in the first step. Subsequent P–SH addition to the O–CR₃ carbon atom, followed by O–CR₃ bond cleavage gives the final product, thiol **2**. To rationalize this mechanism for the formation of the thiols **2**, the reaction of optically active 1-phenylethanol and LR was carried out. Treatment of (*S*)-(-)-1-phenylethanol (*S*)-**1f** { $[\alpha]_D -45.27$ (CHCl₃)} with LR in toluene at reflux temperature yielded (*S*)-(-)-1-phenylethanethiol (*S*)-**2f** { $[\alpha]_D -85.01$ (CHCl₃)}. Thus the conversion of

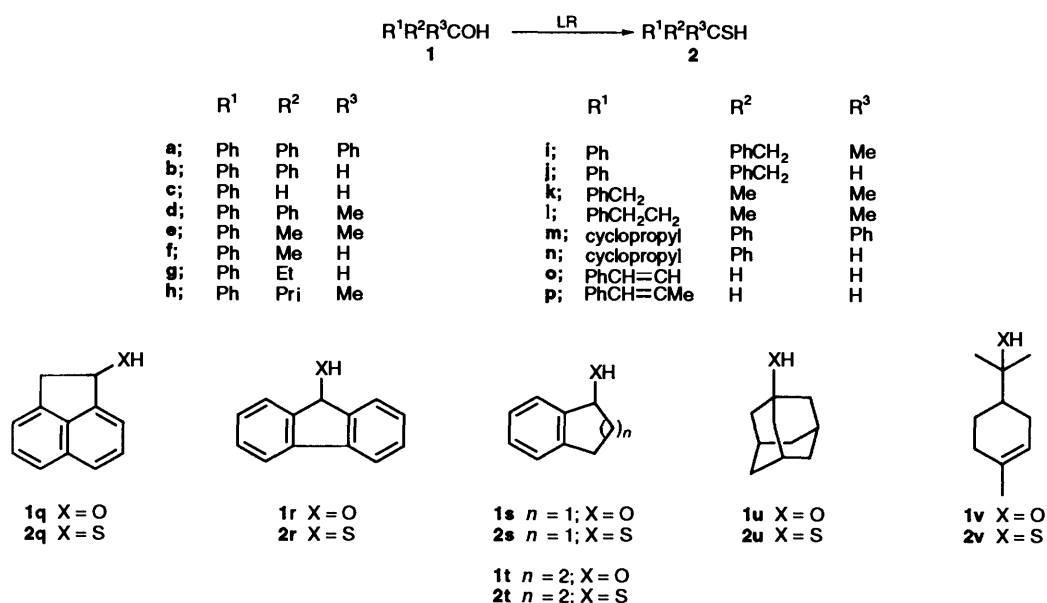
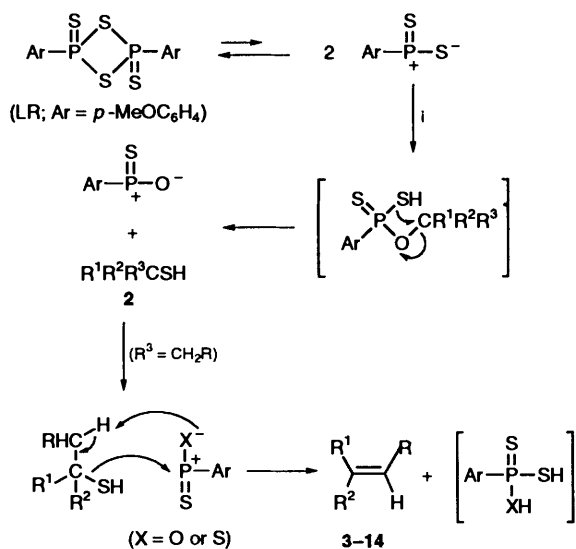


Table 1 Yields of the thiols 2

	Solvent	Molar quotient 1/LR	Time (t/h)	Yield (%) 2 ^a	
				2	Other products
1a	DME ^{b,c}	2	15	100	
	DME ^c	2	5	87	
	DME ^d	2	1	82	
	Toluene ^d	2	0.2	100	
1b	Toluene ^d	1	0.5	94	
1c	Toluene ^d	1	48	55	
1d	DME ^c	1	3	77	Ph ₂ C=CH ₂ 3 13
	Toluene ^d	1	0.5	7	3 91
1e	Toluene ^d	1	3	39	PhC(Me)=CH ₂ 4 trace
1f	Toluene ^d	1	0.5	25	
1g	Toluene ^d	2	6	45	
1h	Toluene ^d	1	0.5	11	
	Toluene ^d	2	0.5	10	
1i	Toluene ^d	1	0.5	23	Ph(Me)C=CH(Ph) 5 60
	Toluene ^d	2	0.5	15	5 38
1j	Toluene ^d	1	0.5	15	PhCH=CHPh 6 trace
	Toluene ^d	2	0.5	12	6 7
1k	DME ^c	1	1	<i>e</i>	
	Toluene ^d	1	0.5	9	PhCH=CMe ₂ 7 17
1l	Toluene ^d	2	0.5	16	PhCH ₂ C(Me)=CH ₂ 8 11
	Toluene ^d	2	0.5	16	PhCH ₂ CH ₂ C(Me)=CH ₂ 9 18
	Toluene ^d	2	0.5	16	PhCH ₂ CH=CMe ₂ 10 36
	Toluene ^d	2	0.5	16	HSCH ₂ CH ₂ CH=CPh ₂ 11 49
1m	Toluene ^d	1	0.5	15	HSCH ₂ CH ₂ CH=CHPh 12 14
1n	Toluene ^d	1	0.5	68	
1o	Toluene ^d	2	2	73	
1p	Toluene ^d	2	1	43	PhCH(SH)C(Me)=CH ₂ 13 15
1q	Toluene ^d	1	0.5	72	Acenaphthylene 14 13
1r	Toluene ^d	1	0.5	18	
1s	Toluene ^d	1	0.5	67	
1t	Toluene ^d	2	0.5	65	
1u	Toluene ^d	1	3	23	
1v	Toluene ^d	2	0.5	20	

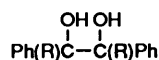
^a Isolated yield. ^b 1,2-Dimethoxyethane. ^c Room temperature. ^d Reflux temperature. ^e No reaction.

Scheme 1 Reagent: i, R¹R²R³COH 1

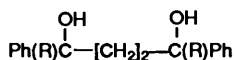
the alcohol **1f** into the thiol **2f** takes place with retention of configuration. Elimination of hydrogen sulfide from the thiols **2** by the mixed *O,S*-phosphine ylide (X = O) thus formed or thiophosphine ylide (X = S) then affords the dehydration products **3-10** and **14**. The former ylide might be more appropriate for the elimination reaction since only 0.5 mole equivalent of LR was used in these reactions. The mechanism for the rearranged products **11-13** involves initial formation of thiol followed by the further rearrangement as shown in Scheme

2 [eqns. (1) and (2)]. The reaction described above provides a simple method for the synthesis of thiols from alcohols. In diol systems which are located 1,2 or 1,4 to each other, the opportunity exists for dehydration or ring closure involving LR to give 1,3-dienes or 5- or 6-membered rings.¹ We also explored the reaction of diols with LR in the hope of the formation of sulfur heterocycles or dienes through the corresponding dithiols. The 1,2-diol benzopinacol **15a** reacted with LR in toluene at reflux temperature to give 1,1-diphenylmethanethiol **2b** after purification by flash chromatography. 2,3-Diphenylbutane-2,3-diol **15b** reacted with LR to give the rearranged thiol **16** (Table 2).

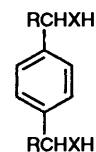
The reaction mechanism almost always involves a dithiol (or hydroxy thiol) intermediate, which then suffers elimination of H₂S (or water) and 1,3-migration of the SH group [Scheme 2, eqn. (3)]. Reaction of 1,4-diols **17** with LR in the same way led to complex mixtures. Work-up by flash chromatography on silica gel allowed the isolation of only one defined product, 1,3-dienes **18**. The formation 1,3-dienes **18** can be explained in terms of a 1,4-dithiol intermediate followed by the elimination of H₂S. *p*-(Dihydroxymethyl)benzene derivatives **19**, in which the two hydroxy groups do not interact with each other, gave dithiols **20**. On the other hand, *o*-(dihydroxymethyl)benzene derivatives **21**, in which two hydroxy groups are located 1,4 to each other, yielded the 1,3-dihydrobenzo[*c*]thiophenes **22** when treated with LR in toluene at reflux temperature. 1,3-Dihydroisobenzofuran **23** was obtained as main product in the case of *o*-(hydroxymethyl)(diphenylhydroxymethyl)benzene **21c**. Treatment of *o*-(mercaptomethyl)(hydroxymethyl)benzene derivatives **24** with LR also gave 1,3-dihydrobenzo[*c*]thiophenes **22a** and **22c**. This result indicates that the initially produced hydroxy thiol undergoes a ring closure giving 1,3-dihydrobenzo[*c*]thiophenes **22**.



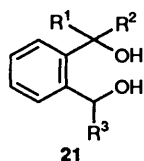
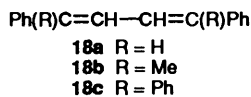
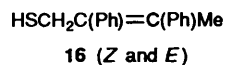
15a R = Ph
15b R = Me



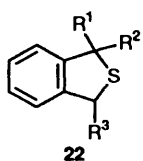
17a R = H
17b R = Me
17c R = Ph



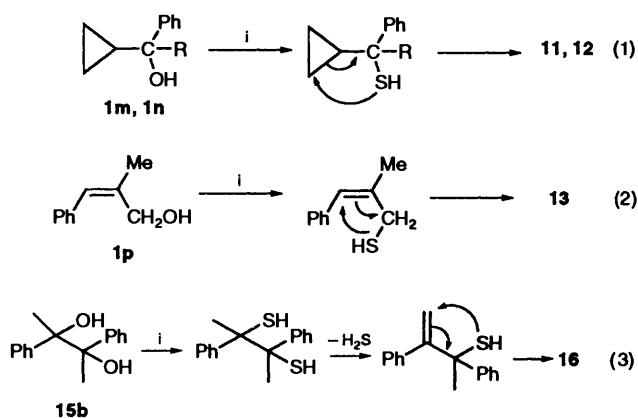
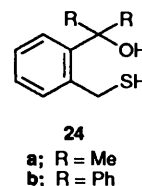
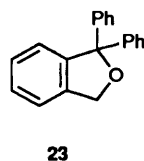
19a R = Me, X = O
19b R = Ph, X = O
20a R = Me, X = S
20b R = Ph, X = S



R¹
a; Me
b; Ph
c; Ph
d; Ph
e; *p*-MeC₆H₄



R²
Me
H
Ph
H
H
p-MeC₆H₄



Scheme 2 Reagent: i, LR

Experimental

M.p.s and b.p.s were measured with a Yanaco micro-melting apparatus and Kugelrohr distillation apparatus, respectively, and are uncorrected. IR spectra were recorded with a Hitachi 260-30 spectrophotometer. ¹H and ¹³C NMR spectra were run on JEOL FX-100 (100 MHz) or FX-90Q (90 MHz) spectrometers in CDCl₃ as solvent with tetramethylsilane as internal standard. *J*-Values are given in Hz.

Reaction of the Alcohols 1 with LR. General Procedure.—A solution of an alcohol **1** (0.002 mol) and LR (0.001–0.002 mol) in toluene or DME (70 cm³) was stirred at room or reflux temperature under argon. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene–hexane (4:1–1:4) as eluent to yield the corresponding thiols **2** and alkenes **3–13**. The thiols **2a** and **2c**, and alkenes **3–7** and **14**, were confirmed by direct comparison of their IR and NMR spectra with those of authentic samples which are commercially available.

Diphenylmethanethiol 2b. B.p. 140 °C at 3 mmHg (lit.,⁷ 135 °C at 1.5 mmHg); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2560; δ_{H} 2.23 (1 H, d, *J* 4.9),

5.40 (1 H, d, *J* 4.9) and 7.07–7.45 (10 H, m); δ_{C} 47.7 (d), 127.1 (d), 127.8 (d), 128.5 (d) and 143.3 (s).

1,1-Diphenylethanethiol 2d B.p. 125 °C at 3 mmHg (Found: C, 78.45; H, 6.65. C₁₄H₁₄S requires C, 78.45; H, 6.55%); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2550; δ_{H} 2.13 (3 H, s), 2.46 (1 H, s) and 7.07–7.83 (10 H, m); δ_{C} 34.7 (q), 53.5 (s), 126.5 (d), 127.0 (d), 128.0 (d) and 148.2 (s).

2-Phenylpropane-2-thiol 2e. B.p. 100 °C at 3 mmHg (lit.,⁸ 63–64 °C at 2.3 mmHg); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2560; δ_{H} 1.81 (6 H, s), 2.22 (1 H, s), 7.10–7.40 (3 H, m) and 7.48–7.61 (2 H, m); δ_{C} 34.6 (q), 45.8 (s), 125.3 (d), 126.5 (d), 128.2 (d) and 148.4 (s).

1-Phenylethanethiol 2f. B.p. 95 °C at 3 mmHg (lit.,⁹ 71–72 °C at 4 mmHg); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2550; δ_{H} 1.64 (3 H, d, *J* 6.8), 1.97 (1 H, d, *J* 5.8), 4.08–4.35 (1 H, m) and 7.14–7.43 (5 H, m); δ_{C} 26.1 (q), 38.7 (d), 126.4 (d), 127.1 (d), 128.6 (d) and 145.8 (s).

1-Phenylpropane-1-thiol 2g. B.p. 105 °C at 3 mmHg (lit.,¹⁰ 106–108 °C at 18 mmHg); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2560; δ_{H} 0.91 (3 H, t, *J* 7.3), 1.89 (1 H, d, *J* 4.9), 1.79–2.10 (2 H, m), 3.77–3.91 (1 H, m) and 7.13–7.39 (5 H, m); δ_{C} 12.5 (q), 18.5 (t), 32.9 (d), 127.0 (d), 127.1 (d), 128.5 (d) and 144.6 (s).

3-Methyl-2-phenylbutane-2-thiol 2h. B.p. 130 °C at 3 mmHg (Found: C, 73.0; H, 9.0. C₁₁H₁₆S requires C, 73.3; H, 8.95%); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2565; δ_{H} 0.78 (3 H, d, *J* 6.8), 1.00 (3 H, d, *J* 6.8), 1.72 (3 H, s), 1.92 (1 H, s), 2.29 (1 H, sep, *J* 6.8) and 7.08–7.59 (5 H, m); δ_{C} 18.1 (q), 18.5 (q), 27.0 (q), 40.1 (d), 54.6 (s), 126.3 (d), 127.9 (d) and 147.5 (s).

1,2-Diphenylpropane-2-thiol 2i. B.p. 165 °C at 3 mmHg (Found: C, 78.85; H, 7.0. C₁₅H₁₆S requires C, 78.9; H, 7.05%); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2560; δ_{H} 1.76 (3 H, s), 2.15 (1 H, s), 3.26 (2 H, dd, *J* 13.2 and 15.2), 6.80–7.00 (2 H, m) and 7.05–7.55 (8 H, m); δ_{C} 30.7 (q), 50.2 (s), 53.0 (t), 126.5 (d), 126.7 (d), 127.6 (d), 128.0 (d), 130.6 (d), 137.2 (s) and 146.2 (s).

1,2-Diphenylethanethiol 2j. B.p. 150 °C at 3 mmHg (Found: C, 78.5; H, 6.55. C₁₄H₁₄S requires C, 78.45; H, 6.55%); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2560; δ_{H} 1.94 (1 H, d, *J* 4.4), 3.08 (1 H, A of ABX, *J* 8.3 and 13.7), 3.28 (1 H, B of ABX, *J* 6.8 and 13.7), 4.15–4.35 (1 H, m) and 7.03–7.56 (10 H, m); δ_{C} 45.8 (q), 46.3 (t), 126.6 (d), 127.1 (d), 127.3 (d), 128.3 (d), 128.5 (d), 129.2 (d), 138.8 (s) and 143.6 (s).

Table 2 Yields of the products derived from the reaction of diols with LR^a

	Molar quotient diol/LR	Yield (%) of products
15a ^b	0.5	2b 53
15b ^b	1	16 21 (Z + E)
17a	1	18a 17
17b	1	18b 26
17c	1	18c 24
19a	1	20a 17
19b	1	20b 52
21a	0.5	22a 10
	1	22a 13
21b	0.5	22b 38
	1	22b 9
21c	1	22c 3, 23 96
21d	1	22d 49
21e	1	22e 55
24a	2	22a 45
24b	2	22c 89

^a Reaction conditions: reflux in toluene for 0.5 h. ^b Reflux in toluene for 3 h.

2-Methyl-1-phenylpropane-2-thiol 2k. B.p. 90 °C at 3 mmHg (Found: C, 72.35; H, 8.55. C₁₀H₁₄S requires C, 72.25; H, 8.5%); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2560; δ_{H} 1.39 (6 H, s), 1.70 (1 H, s), 2.89 (2 H, s) and 7.27 (5 H, br s); δ_{C} 32.4 (q), 44.8 (s), 52.5 (t), 126.5 (d), 127.8 (d), 130.8 (d) and 137.8 (s).

The alkenes **7** and **8** could not be separated completely.

2-Methyl-3-phenylprop-1-ene 8.¹¹ δ_{H} 1.67 (3 H, s), 3.31 (2 H, s), 4.77 (2 H, br d) and 7.05–7.40 (5 H, m); δ_{C} 22.1 (q), 44.7 (t), 111.9 (t), 126.1 (d), 128.3 (d), 128.9 (d), 138.7 (s) and 139.8 (s).

2-Methyl-4-phenylbutane-2-thiol 2l. B.p. 110 °C at 3 mmHg (Found: C, 73.6; H, 9.05. C₁₁H₁₆S requires C, 73.3; H, 8.95%); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2560; δ_{H} 1.44 (6 H, s), 1.74 (1 H, s), 1.78–1.96 (2 H, m), 2.67–2.85 (2 H, m) and 7.08–7.39 (5 H, m); δ_{C} 31.9 (t), 32.8 (q), 44.6 (s), 48.6 (t), 125.8 (d), 128.4 (d) and 142.2 (s).

The alkenes **9** and **10** could not be separated completely.

2-Methyl-4-phenylbut-1-ene 9.¹² δ_{H} 1.76 (3 H, s), 2.22–2.39 (2 H, m), 2.67–2.85 (2 H, m), 4.72 (2 H, br s) and 7.06–7.37 (5 H, m); δ_{C} 25.7 (q), 34.3 (t), 34.4 (t), 110.2 (t), 123.2 (d), 125.7 (d), 128.3 (d), 132.5 (s) and 141.8 (s).

3-Methyl-1-phenylbut-2-ene 10.¹³ δ_{H} 1.72 (3 H, s), 1.73 (3 H, s), 3.34 (2 H, br d, J 7.3), 5.33 (1 H, br t, J 7.3) and 7.06–7.37 (5 H, m); δ_{C} 17.8 (q), 26.6 (q), 39.6 (t), 123.2 (d), 125.7 (d), 128.3 (d), 142.2 (s) and 145.3 (s).

Cyclopropyl(diphenyl)methanethiol 2m. B.p. 185 °C at 3 mmHg (Found: C, 80.15; H, 6.85. C₁₆H₁₆S requires C, 79.95; H, 6.7%); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2560; δ_{H} 0.29–0.74 (4 H, A₂B₂ m), 1.59–1.87 (1 H, m), 2.24 (1 H, s) and 7.10–7.72 (10 H, m); δ_{C} 3.3 (t), 23.8 (d), 59.0 (s), 126.7 (d), 127.7 (d), 128.4 (d) and 147.0 (s).

4,4-Diphenylbut-3-ene-1-thiol 11. B.p. 165 °C at 3 mmHg (Found: C, 80.1; H, 6.65. C₁₆H₁₆S requires C, 79.95; H, 6.7%); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2560; δ_{H} 1.37 (1 H, t, J 6.8), 2.24–2.74 (4 H, m), 6.06 (1 H, t, J 6.8) and 7.11–7.52 (10 H, m); δ_{C} 24.7 (t), 33.9 (t), 126.0 (d), 126.7 (d), 127.1 (d), 127.2 (d), 128.1 (d), 128.2 (d), 130.0 (d), 139.8 (s), 142.3 (s) and 143.6 (s).

Cyclopropyl(phenyl)methanethiol 2n and **4-phenylbut-3-ene-1-thiol 12** could not be separated completely. B.p. (a mixture of **2n** and **12**) 115 °C at 3 mmHg (Found: C, 72.85; H, 7.35. C₁₀H₁₂S requires C, 73.15; H, 7.35%); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2560; δ_{H} (for **2n**) 0.20–0.85 (4 H, m), 1.20–1.56 (1 H, m), 2.04 (1 H, d), 3.38 (1 H, dd, J 4.4 and 9.3) and 7.15–7.47 (5 H, m); (for **12**) 2.42–2.76 (4 H, m), 6.15 (1 H, td, J 5.8 and 15.6), 6.42 (1 H, d, J 15.6) and 7.15–7.47 (5 H, m); δ_{C} (for **2n**) 6.0 (t), 6.4 (t), 20.1 (d), 49.4 (d), 127.0 (d), 127.1 (d), 128.5 (d) and 144.0 (s); (for **12**) 24.3 (t), 37.2 (t), 126.1 (d), 128.5 (d), 132.1 (d) and 137.2 (s).

3-Phenylprop-2-ene-1-thiol 2o. B.p. 130 °C at 3 mmHg (lit.,¹⁴ 124–125 °C at 13 mmHg); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2560; δ_{H} 1.50 (1 H, t, J 7.8), 3.32 (2 H, dd, J 6.3 and 7.8), 6.23 (1 H, dd, J 6.3 and 15.6), 6.44 (1 H, d, J 15.6) and 7.10–7.42 (5 H, m); δ_{C} 27.3 (t), 126.3 (d), 127.6 (d), 128.5 (d), 128.7 (d), 130.8 (d) and 136.7 (s).

2-Methyl-3-phenylprop-2-ene-1-thiol 2p. B.p. 130 °C at 3 mmHg (Found: C, 73.05; H, 7.4. C₁₀H₁₂S requires C, 73.15; H, 7.35%); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2550 and 1640; δ_{H} 1.52 (1 H, t, J 7.8), 1.98 (3 H, d, J 1.5), 3.29 (2 H, dd, J 1.0 and 7.8), 6.43 (1 H, br s) and 7.09–7.43 (5 H, m); δ_{C} 16.5 (q), 34.8 (d), 126.4 (d), 128.1 (d), 128.8 (d), 137.4 (s) and 137.6 (s).

2-Methyl-1-phenylprop-2-ene-1-thiol 13. B.p. 135 °C at 3 mmHg (Found: C, 73.15; H, 7.35%); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2550 and 1635; δ_{H} 1.73 (3 H, s), 1.93 (1 H, d, J 5.4), 4.73 (1 H, d, J 5.4), 4.94 (1 H, t, J 1.0), 5.17 (1 H, s) and 7.13–7.42 (5 H, m); δ_{C} 20.1 (q), 49.9 (d), 113.0 (t), 127.1 (d), 127.5 (d), 128.4 (d), 141.7 (s) and 146.3 (s).

Acenaphthene-1-thiol 2q. B.p. 150 °C at 3 mmHg (Found: C, 77.45; H, 5.4. C₁₂H₁₀S requires C, 77.4; H, 5.4%); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2550; δ_{H} 2.10 (1 H, d, J 7.8), 3.31 (1 H, dd, J 3.4 and 16.6), 3.93 (1 H, dd, J 7.8 and 16.6), 4.75 (1 H, dd, J 3.4 and 7.8) and 7.15–7.68 (6 H, m); δ_{C} 39.8 (d), 44.1 (t), 119.5 (d), 122.7 (d), 123.7 (d), 128.1 (d), 131.2 (s), 136.8 (s), 141.9 (s) and 147.5 (s).

Fluorene-9-thiol 2r. M.p. 101–102 °C (lit.,¹⁵ 103–106 °C); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2540; δ_{H} 2.02 (1 H, d, J 9.3), 4.91 (1 H, d, J 9.3), 7.20–7.46 (4 H, m) and 7.53–7.78 (4 H, m); δ_{C} 42.6 (d), 119.9 (d), 125.1 (d), 127.6 (d), 128.0 (d), 139.5 (s) and 147.0 (s).

Indane-1-thiol 2s. B.p. 115 °C at 3 mmHg (Found: C, 72.05; H, 6.75. C₉H₁₀S requires C, 71.95; H, 6.7%); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2555; δ_{H} 1.83 (1 H, d, J 7.3), 1.83–2.20 (1 H, m), 2.42–3.24 (3 H, m), 4.37 (1 H, q, J 7.3) and 7.07–7.57 (4 H, m); δ_{C} 30.8 (t), 38.0 (t), 42.3 (d), 124.3 (d), 124.5 (d), 126.8 (d), 127.4 (d), 142.5 (s) and 145.9 (s).

1,2,3,4-Tetrahydronaphthalene-1-thiol 2t. B.p. 120 °C at 3 mmHg (Found: C, 73.3; H, 7.45. C₁₀H₁₂S requires C, 73.15; H, 7.35%); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2550; δ_{H} 1.60–2.39 (4 H, m), 1.95 (1 H, d, J 6.8), 2.68–3.00 (2 H, m), 4.22–4.44 (1 H, m), 6.96–7.24 (3 H, m) and 7.28–7.42 (1 H, m); δ_{C} 18.9 (t), 29.1 (t), 33.7 (t), 38.2 (d), 125.9 (d), 126.7 (d), 129.2 (d), 129.8 (d), 136.1 (s) and 138.9 (s).

Adamantane-1-thiol 2u. B.p. 100 °C at 3 mmHg (sublimation) (lit.,¹⁶ m.p. 100–102 °C); δ_{H} 1.57–1.75 (7 H, m) and 1.83–2.10 (9 H, m); δ_{C} 30.2 (d), 35.9 (t), 43.3 (s) and 47.6 (t).

2-(4-Methylcyclohex-3-enyl)propane-2-thiol 2v. B.p. 95 °C at 3 mmHg (lit.,¹⁷ 40 °C at 0.0001 mmHg); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1640; δ_{H} 1.34 (3 H, s), 1.40 (3 H, s), 1.55 (1 H, s), 1.66 (3 H, br s), 1.45–2.04 (2 H, m), 1.81–2.22 (5 H, m) and 5.38 (1 H, br d); δ_{C} 23.2 (q), 24.9 (t), 27.4 (t), 30.1 (q), 31.1 (t), 31.4 (q), 45.9 (d), 47.9 (s), 120.5 (d) and 133.8 (s).

Reaction of the Diols with LR. General Procedure.—A solution of a diol (0.002 mol) and LR (0.001–0.004 mol) in toluene (70 cm³) was refluxed under argon for 0.5–3 h. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene–hexane (4:1–1:4) to give the products **2b**, **16**, **18**, **20**, **22** and **23**. The dienes **18a** and **18c** were confirmed by direct comparison of their IR and NMR spectra with those of commercially available authentic materials.

(E)-2,3-Diphenylbut-2-ene-1-thiol (E)-16. M.p. 59–60 °C (Found: C, 79.8; H, 6.75. C₁₆H₁₆S requires C, 79.95; H, 6.7%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2550; δ_{H} 1.38 (1 H, t, J 7.8), 1.86 (3 H, s), 3.32 (2 H, d, J 7.8) and 7.17–7.50 (10 H, m); δ_{C} 22.8 (q), 29.3 (t), 126.8 (d), 127.7 (d), 128.2 (d), 128.4 (d), 129.2 (d), 135.7 (s), 136.3 (s), 140.5 (s) and 143.2 (s).

(Z)-2,3-Diphenylbut-2-ene-1-thiol (Z)-16. B.p. 150 °C at 3 mmHg; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2560; δ_{H} 1.56 (1 H, t, J 7.3), 2.22 (3 H, s), 3.64 (2 H, d, J 7.3) and 6.90–7.43 (10 H, m); δ_{C} 20.9 (q), 28.7 (t), 126.0 (d), 126.2 (d), 127.5 (d), 128.9 (d), 129.7 (d), 135.4 (s), 136.5 (s), 141.3 (s) and 143.5 (s).

2,5-Diphenylhexa-2,4-diene **18b**. M.p. 134–137 °C (lit.,¹⁸ 133–135 °C); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1620; δ_{H} 2.25 (6 H, s), 6.82 (2 H, s) and 7.18–7.60 (10 H, m); δ_{C} 16.2 (q), 123.9 (d), 125.7 (d), 127.0 (d), 128.3 (d), 136.8 (s) and 143.7 (s).

1,1'-(p-Phenylene)diethanethiol **20a**. M.p. 43–44 °C (Found: C, 60.8; H, 7.2. $\text{C}_{10}\text{H}_{14}\text{S}_2$ requires C, 60.55; H, 7.1%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2540; δ_{H} 1.64 (6 H, d, *J* 7.3), 1.97 (2 H, d, *J* 4.9), 4.04–4.36 (2 H, m) and 7.30 (4 H, s); δ_{C} 26.0 (q), 38.2 (d), 126.5 (d) and 144.6 (s).

α,α' -Diphenyl- α,α' -(p-phenylene)dimethanethiol **20b**. M.p. 108–110 °C (Found: C, 74.35; H, 5.55. $\text{C}_{20}\text{H}_{18}\text{S}_2$ requires C, 74.55; H, 5.6%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2530; δ_{H} 2.24 (2 H, d, *J* 4.8), 5.39 (2 H, d, *J* 4.8) and 7.12–7.46 (14 H, m); δ_{C} 47.4 (d), 127.2 (d), 127.7 (d), 127.9 (d), 128.5 (d), 142.3 (s) and 143.1 (s).

1,1-Dimethyl-1,3-dihydrobenzo[c]thiophene **22a**. B.p. 90 °C at 3 mmHg (Found: C, 73.15; H, 7.5. $\text{C}_{10}\text{H}_{12}\text{S}$ requires C, 73.15; H, 7.35%); δ_{H} 1.69 (6 H, s), 4.20 (2 H, s) and 7.11–7.30 (4 H, m); δ_{C} 32.8 (q), 35.5 (t), 57.9 (s), 122.2 (d), 124.7 (d), 126.6 (d), 126.9 (d), 139.7 (s) and 149.8 (s).

1-Phenyl-1,3-dihydrobenzo[c]thiophene **22b**. B.p. 145 °C at 3 mmHg (lit.,¹⁹ 135–140 °C at 0.1 mmHg; m.p. 60–62 °C); δ_{H} 4.18–4.53 (2 H, m), 5.76 (1 H, br s) and 6.86–7.39 (9 H, m); δ_{C} 37.7 (t), 57.8 (d), 124.5 (d), 125.4 (d), 126.9 (d), 127.3 (d), 128.2 (d), 128.5 (d), 140.5 (s), 143.9 (s) and 144.0 (s).

1,1-Diphenyl-1,3-dihydrobenzo[c]thiophene **22c**. M.p. 112–113 °C (Found: C, 83.55; H, 5.5. $\text{C}_{20}\text{H}_{16}\text{S}$ requires C, 83.3; H, 5.6%); δ_{H} 4.19 (2 H, s) and 6.95–7.47 (14 H, m); δ_{C} 36.3 (t), 72.7 (s), 124.7 (d), 126.5 (d), 126.7 (d), 127.8 (d), 128.9 (d), 141.2 (s), 146.0 (s) and 147.3 (s); *m/z* 288 (M^+) and 211 ($\text{M}^+ - \text{C}_6\text{H}_5$).

1,3-Diphenyl-1,3-dihydrobenzo[c]thiophene **22d**. B.p. 200 °C at 3 mmHg (lit.,²⁰ m.p. 130–131 °C); δ_{H} 5.85 (2 H, s) and 6.80–7.60 (14 H, m); δ_{C} 57.4 (d), 125.5 (d), 127.2 (d), 127.4 (d), 127.5 (d), 128.1 (d), 128.6 (d), 129.0 (d), 129.2 (d), 142.8 (s) and 144.5 (s).

1,1-Diphenyl-1,3-dihydrobenzo[c]furan **23**. M.p. 83–85 °C (lit.,²¹ 86–87 °C); δ_{H} 5.17 (2 H, s) and 7.19–7.42 (14 H, m); δ_{C} 71.4 (t), 93.0 (s), 121.1 (d), 123.8 (d), 127.2 (d), 127.3 (d), 127.6 (d), 128.0 (d), 128.3 (d), 139.6 (s), 144.1 (s) and 144.6 (s); *m/z* 272 (M^+) and 195 ($\text{M}^+ - \text{C}_6\text{H}_5$).

1,3-Di-(p-tolyl)-1,3-dihydrobenzo[c]thiophene **22e**. M.p. 99–

100 °C (Found: C, 83.85; H, 6.45. $\text{C}_{22}\text{H}_{20}\text{S}$ requires C, 83.5; H, 6.35%); δ_{H} 2.33 (6 H, s), 5.81 (2 H, s), 7.12–7.19 (6 H, m) and 7.28–7.37 (6 H, m); δ_{C} 21.1 (q), 57.1 (d), 125.4 (d), 127.1 (d), 128.3 (d), 128.9 (d), 129.2 (d), 137.2 (s), 139.9 (s) and 144.6 (s).

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